Accelerated Molecular Dynamics Methods

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Multi-algorithm Methods for Multiscale Simulations
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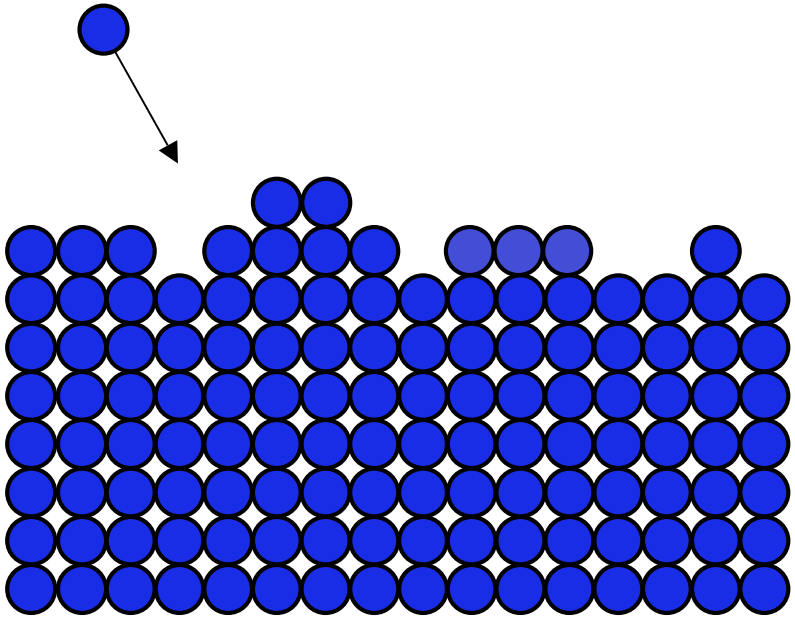
Intel

Outline

- The time scale problem
- The accelerated molecular dynamics concept
- Parallel-replica dynamics
  - Ag(111) island/island decay at T=400K
  - H2 in fullerene lattice
- Temperature accelerated dynamics (TAD)
  - Crystal growth at experimental deposition rates
  - Buckyball/nanotube simulations
  - Radiation damage annealing in MgO
- Summary

Film or Crystal Growth



Deposition event takes ~2 ps

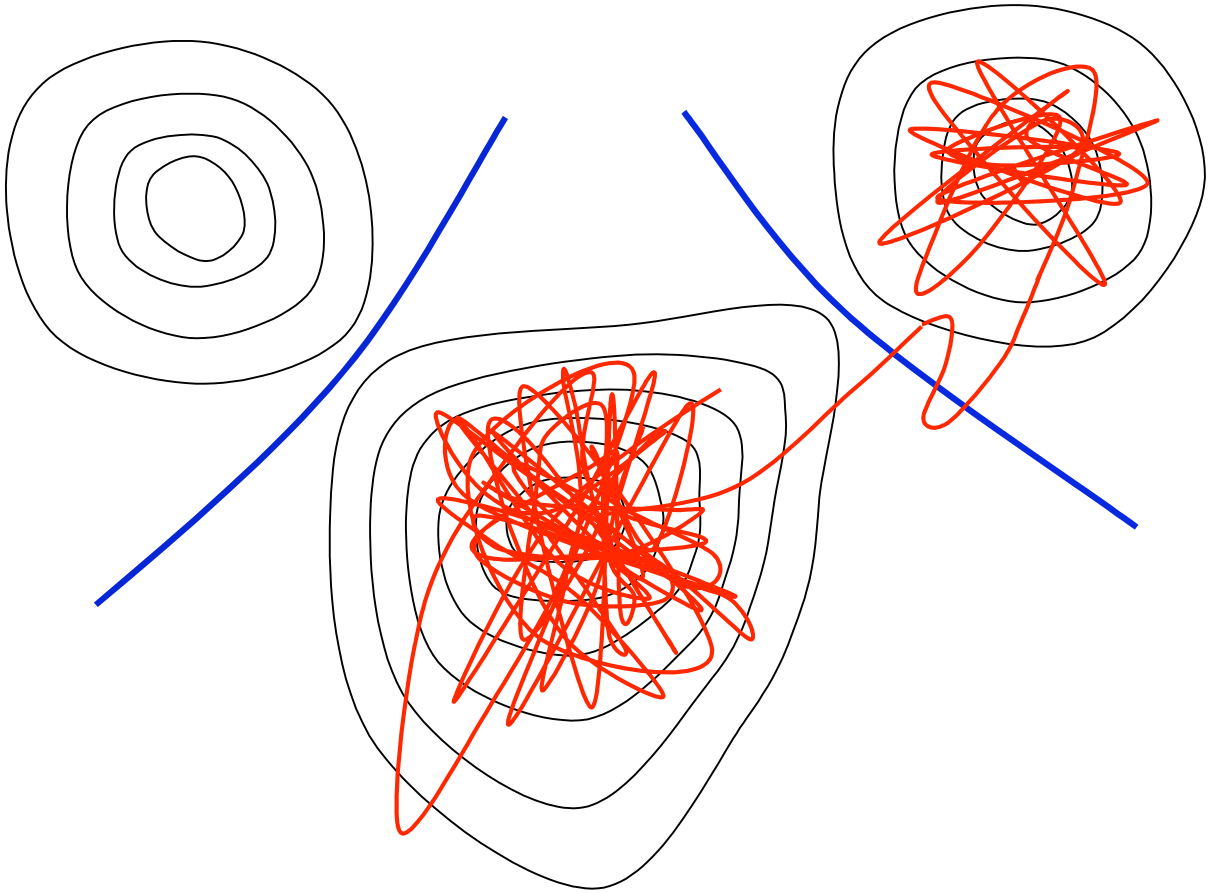
– use molecular dynamics (can reach ns)

Time to next deposition is ~1 s

- diffusion events affect the film morphology
- mechanisms can be surprisingly complex

--> need another approach to treat these

Infrequent Event System



The system vibrates in 3-N dimensional basin many times before finding an escape path. The trajectory finds an appropriate way out (i.e., proportional to the rate constant) without knowing about any of the escape paths except the one it first sees. Can we exploit this?

Accelerated dynamics concept

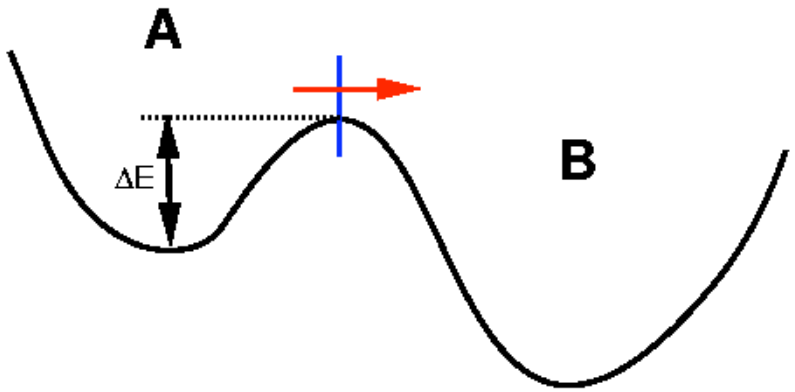
Let the trajectory, which is smarter than we are, find an appropriate way out of each state, The key is to coax it into doing so more quickly, using sound statistical mechanical concepts.

With these accelerated dynamics methods, we can follow a system from state to state, reaching time scales that we may never be able to reach with molecular dynamics.

Often, even just one of these long trajectories can reveal key system behavior. If desired, we can go back through the trajectory to determine rates and properties in more detail, using conventional methods, and/or we can run more long trajectories to gather statistics.

Using these methods, almost every system we have taken to a long time scale has behaved in a way that surprised us.

Transition State Theory (TST)



TST escape rate = equilibrium flux through dividing surface at x=q

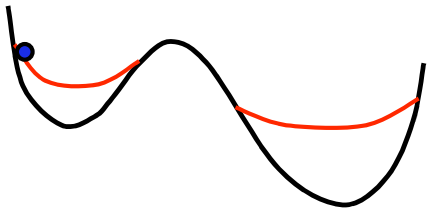
$$k_{A\to B}^{TST} = \int \delta(x - q)\,|\dot{x}|\,$$ (exact flux)

$$k_{A\to B}^{HTST} = \nu_0 e^{-\Delta E/k_B T}$$ (harmonic approx.)

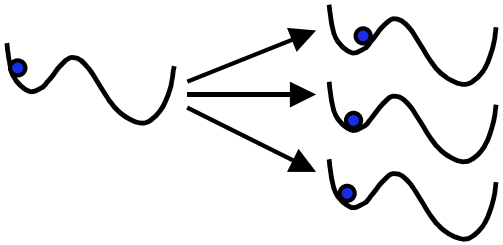
- classically exact rate if no recrossings or correlated events
- no dynamics required
- excellent approximation for materials diffusion
- traditional use of TST requires knowing dividing surface
- can also exploit TST formalism to develop methods that do not require knowing in advance where the dividing surface is

Accelerated Molecular Dynamics Methods

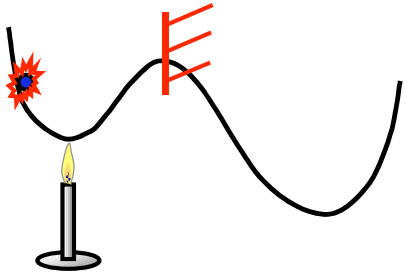
Hyperdynamics (1997)



Parallel Replica Dynamics (1998)



Temperature Accelerated Dynamics (2000)



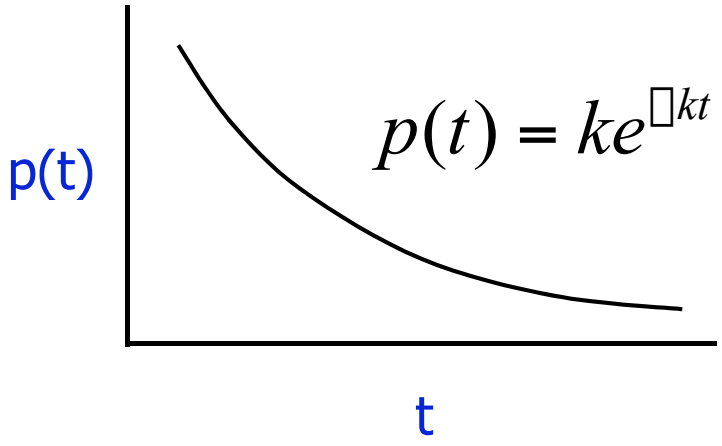
Parallel Replica Dynamics

Parallelizes time evolution

Assumptions:

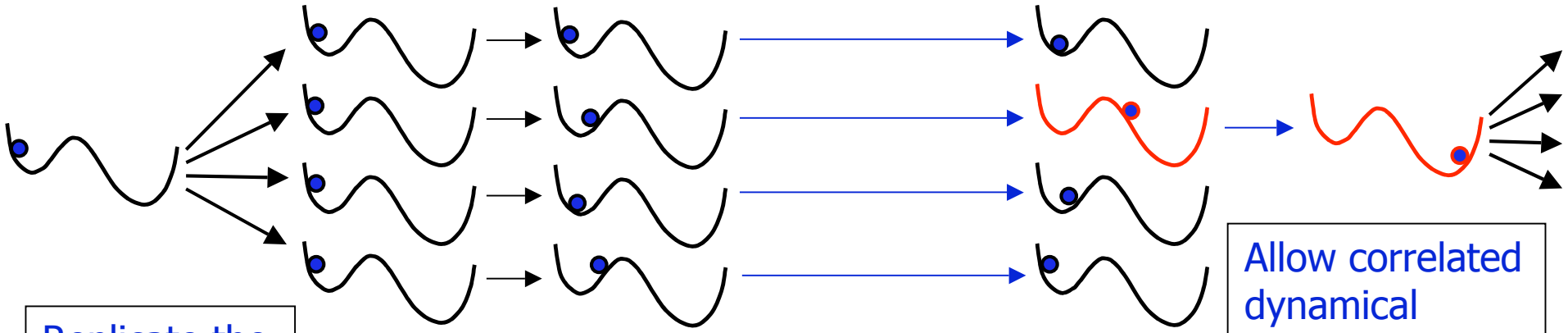
- infrequent events

- exponential distribution of first-escape times



AFV, Phys. Rev. B, 57, R13985 (1998)

Parallel Replica Dynamics Procedure



Replicate the system on M processors

Independently thermalize each of the systems ($\Box_{dephase}$).

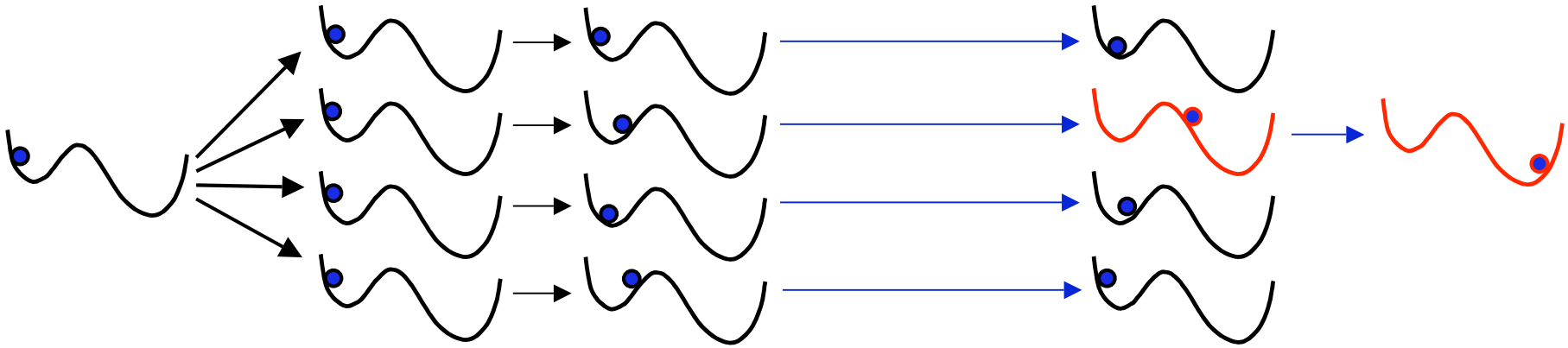
Run MD on all systems until transition occurs one some processor.

Sum up the MD times (t_{sum}).

Allow correlated dynamical events ($\Box_{corr}$).

Then start all over again from the new state.

Parallel Replica Dynamics



The summed time (t_{sum}) obeys the correct exponential distribution, and the system escapes to an appropriate state.

State-to-state dynamics are thus correct; $\Box_{corr}$ stage even releases the TST assumption [AFV, Phys. Rev. B, 57, R13985 (1998)].

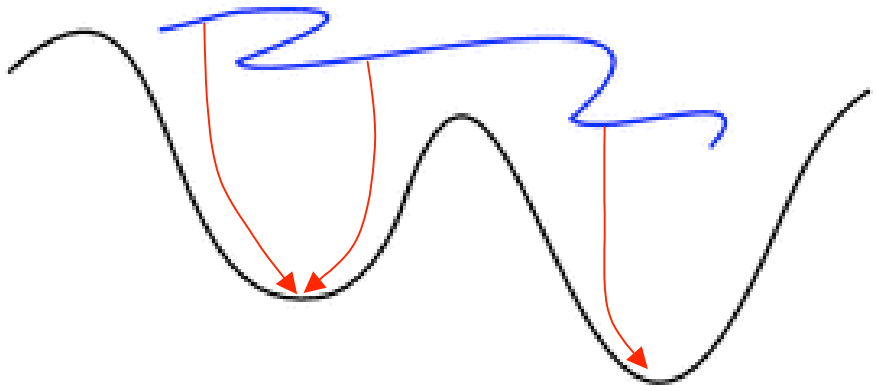
Good parallel efficiency if $\Box_{rxn} / M >> \Box_{dephase} + \Box_{corr}$

Applicable to any system with exponential first-event statistics

Detecting a transition

- best method depends on the system

- simple method for EAM metal systems:
  periodically perform steepest-descent quench;
  see if geometry at basin minimum has changed



Parallel-replica dynamics example

Ag(111) island-on-island decay

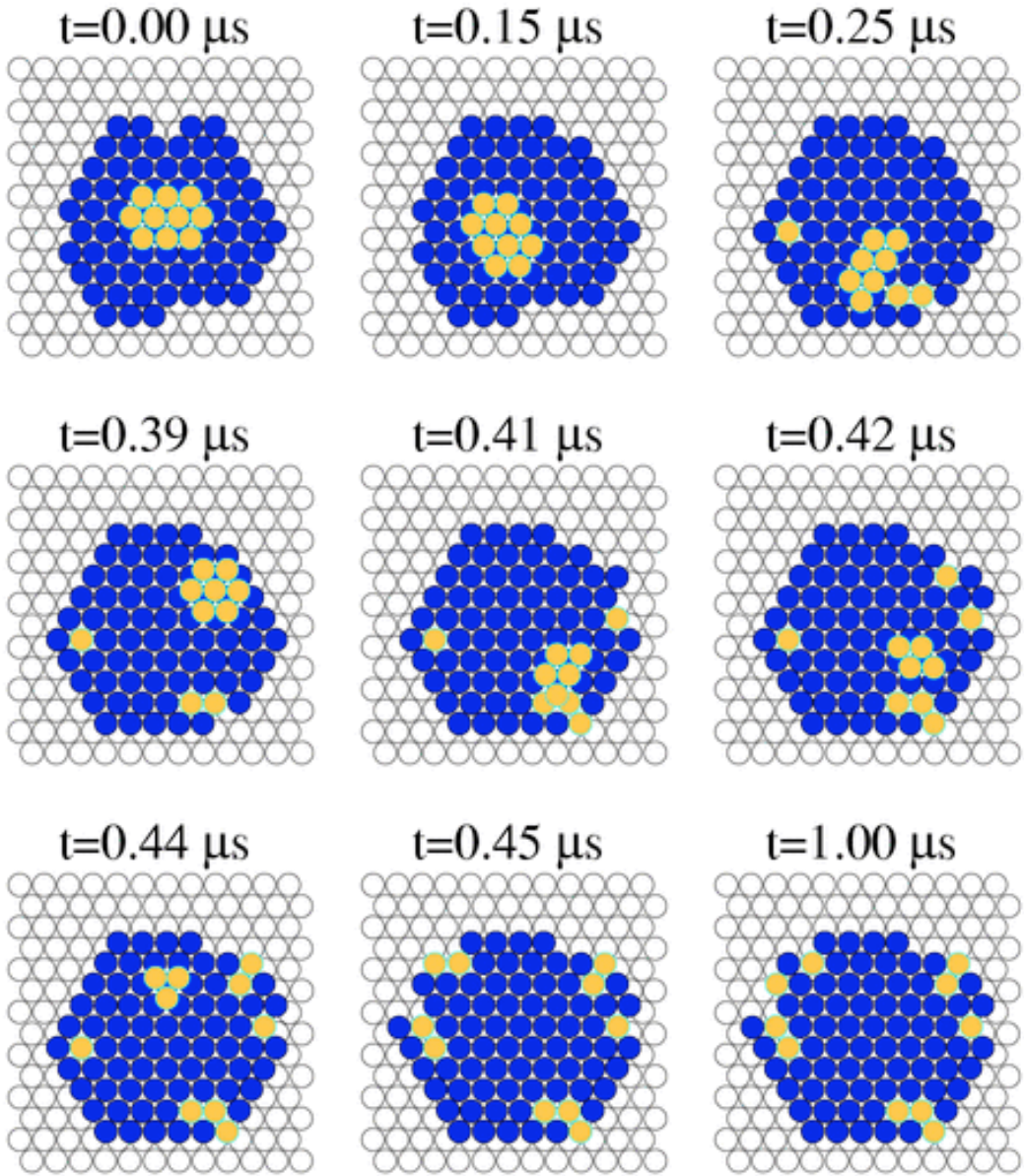
Embedded atom (EAM) potential

Temperature = 400K

5 days on 32 processors
(1 GHz Pentium-IIIs)

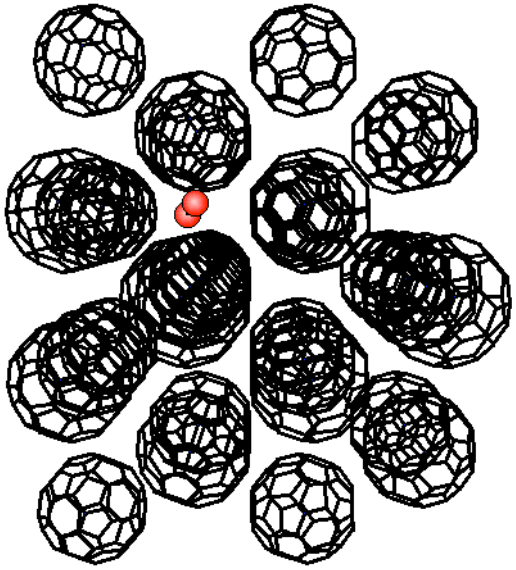
Upper island decays into lower island via step-edge exchange events.

For this case, parallel replica is even faster than temperature-accelerated dynamics, since barriers are low relative to T.



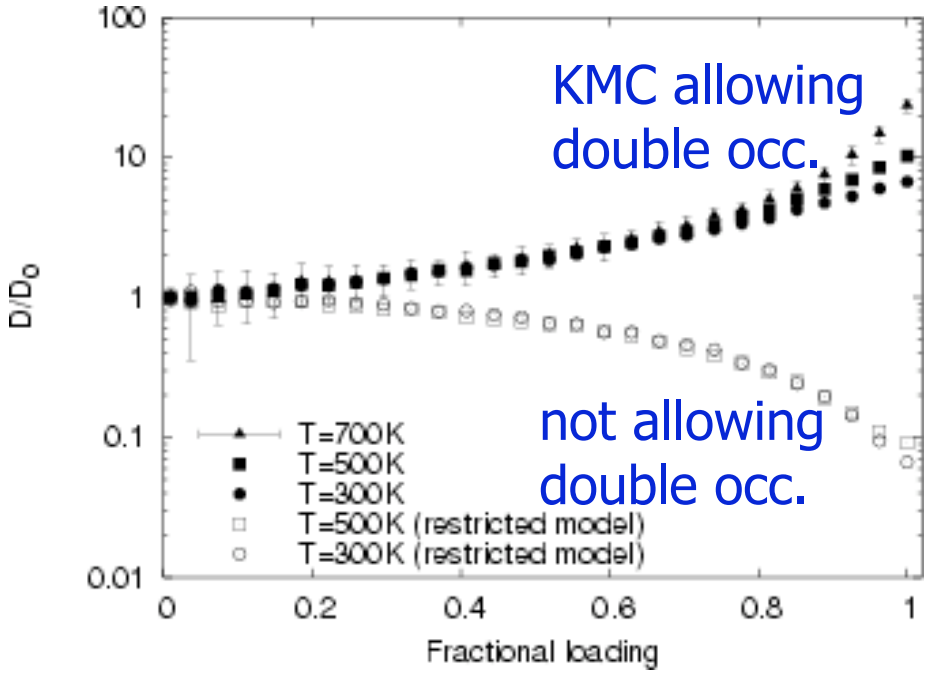
AFV, F. Montalenti and T.C. Germann, Ann. Rev. Mater. Res. 32, 321 (2002).

Interstitial H_2 in FCC fullerene lattice



Parallel-replica simulation revealed unexpected double occupancy of stable site (two H_2 molecules in one octahedral site).

Significant effect on self diffusivity:



Uberuaga, Voter, Sieber and Sholl, Phys. Rev. Lett. 91, 105901 (2003)

TAD

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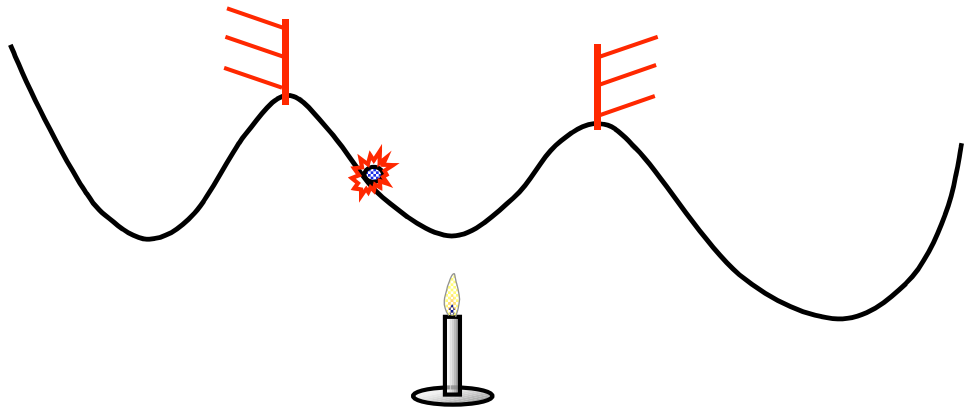
Temperature Accelerated Dynamics (TAD)



Concept:

Raise temperature of system to make events occur more frequently.
Intercept each attempted escape and extrapolate time to low T.

After a few attempted events, we know with desired confidence which one would have occurred first at low temperature -- accept that event.

Correct dynamics within following assumptions:

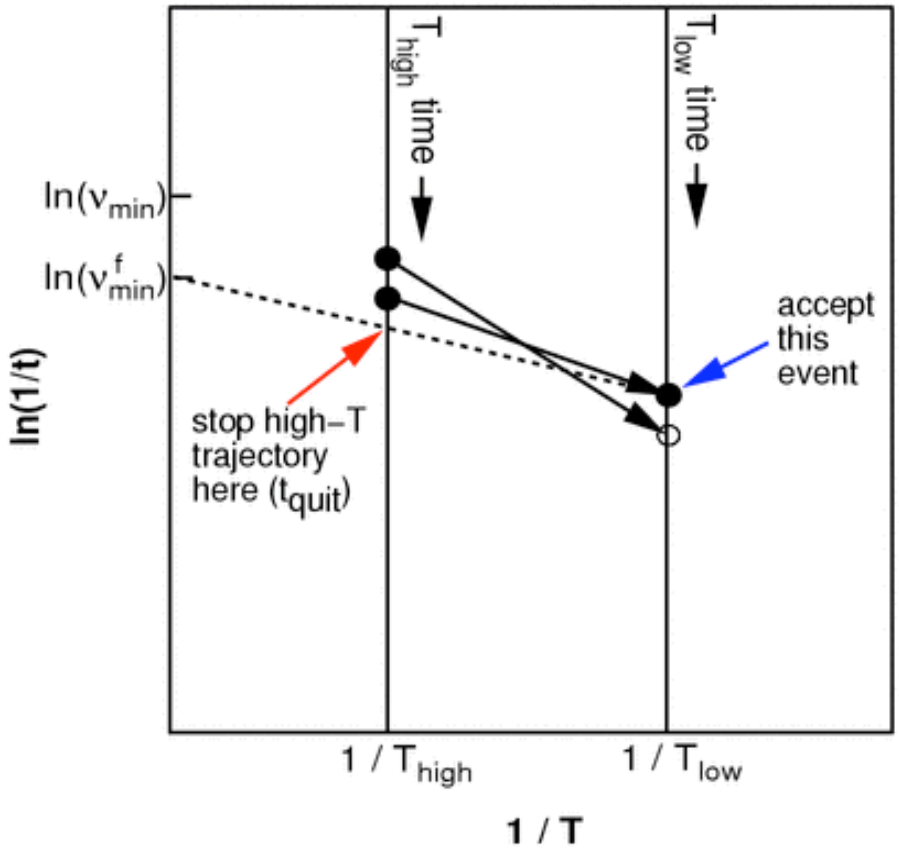
- infrequent-event system
- transition state theory (no correlated events)
- harmonic transition state theory (gives Arrhenius behavior)

$$k = \nu_0 \exp[-\Delta E/k_B T]$$

- all preexponentials (ν_0) are greater than ν_{min}

[Sørensen and Voter, J. Chem. Phys. 112, 9599 (2000)]

TAD - when we can stop the MD and accept an event



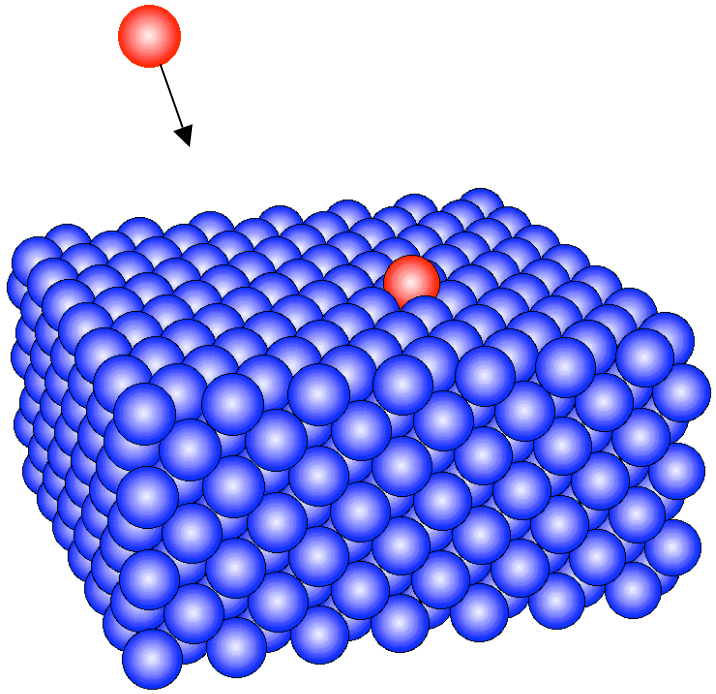
– after time t_{quit}, with confidence f, no new event can replace the first low–T event ($\nu^f_{min} = \nu_{min}/\ln[1/(1-f)]$).

– move along first–event pathway to new basin, start again.

– exact dynamics, assuming harmonic TST, ν_{min}, confidence f

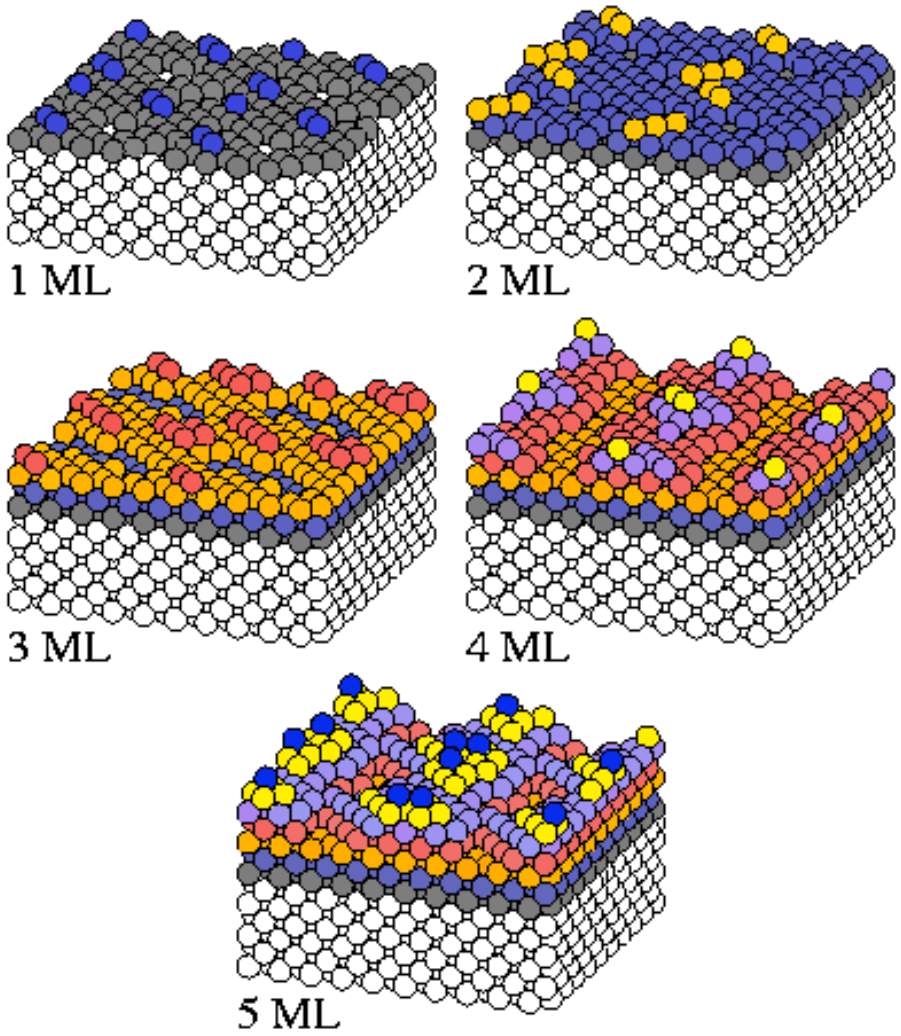
MD+TAD metal deposition simulation

- MD for each deposition event (2 ps)
- TAD for intervening time (~1 s)
- Embedded atom method (EAM) for fcc metals (e.g., Cu, Ag, …; LANL fit)



MD+TAD deposition of Cu/Cu(100)

T=77K, flux= 0.04 ML/s, matching deposition conditions of Egelhoff and Jacob (1989).



boost factor ~10^7

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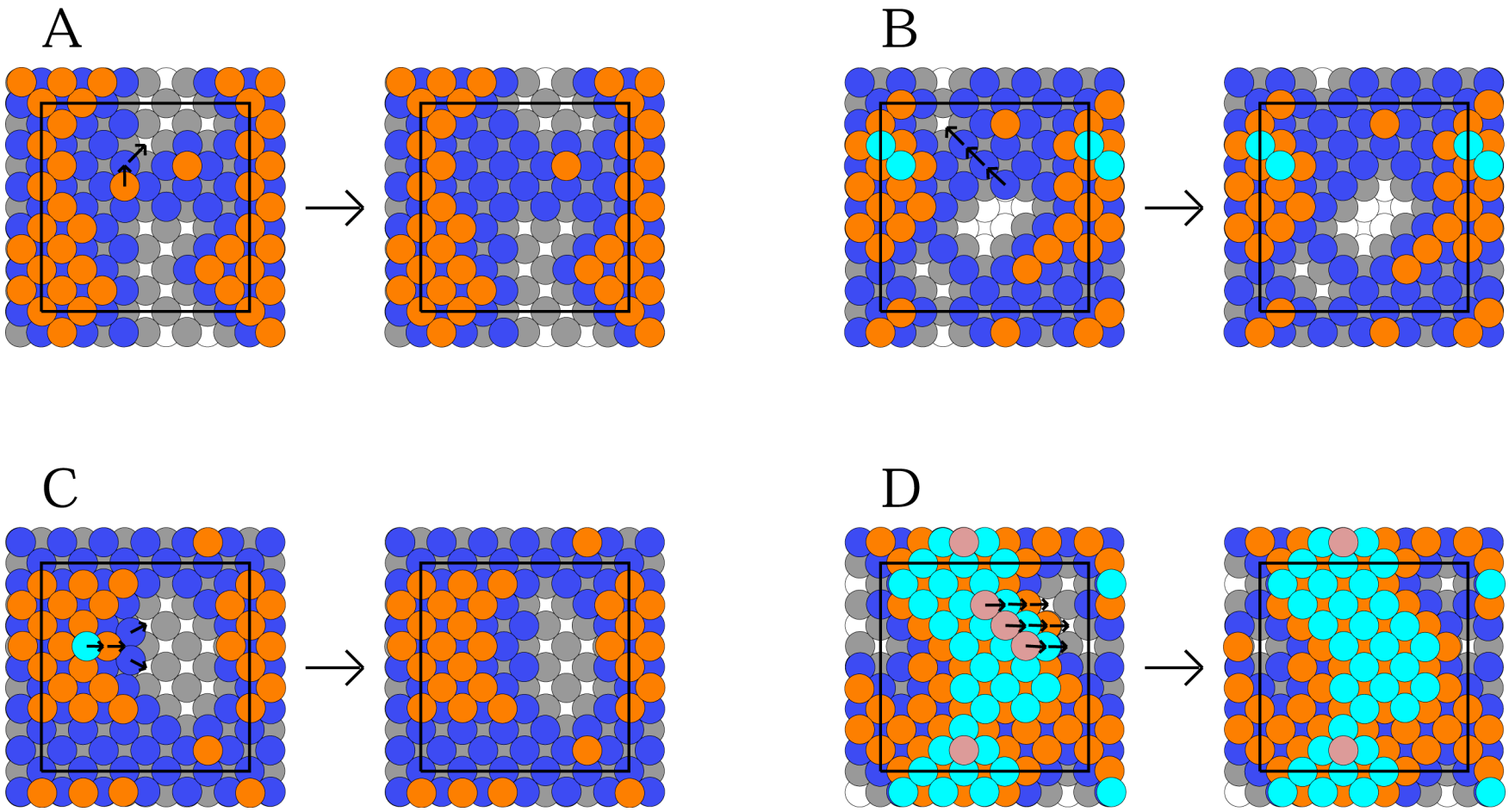
MD+TAD deposition of Cu/Cu(100)

Concerted events observed at T=77K and T=100K:



8-atom cluster sliding on (111) facet (!)

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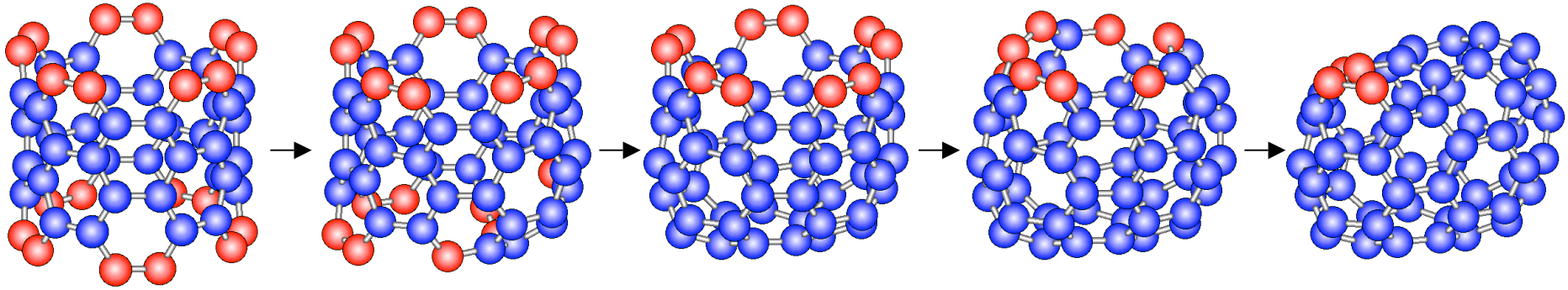
Slice of a nanotube evolved with TAD

60-atom slice - prototype for fragment formed in laser ablation.
Will it form a buckyball when allowed to anneal at T=1500K?

High Temperature: 3000K
Boost: 129



t=0 t=14 □s

Closed object, but not a buckyball (on this time scale).

Uberuaga et al, to be published.

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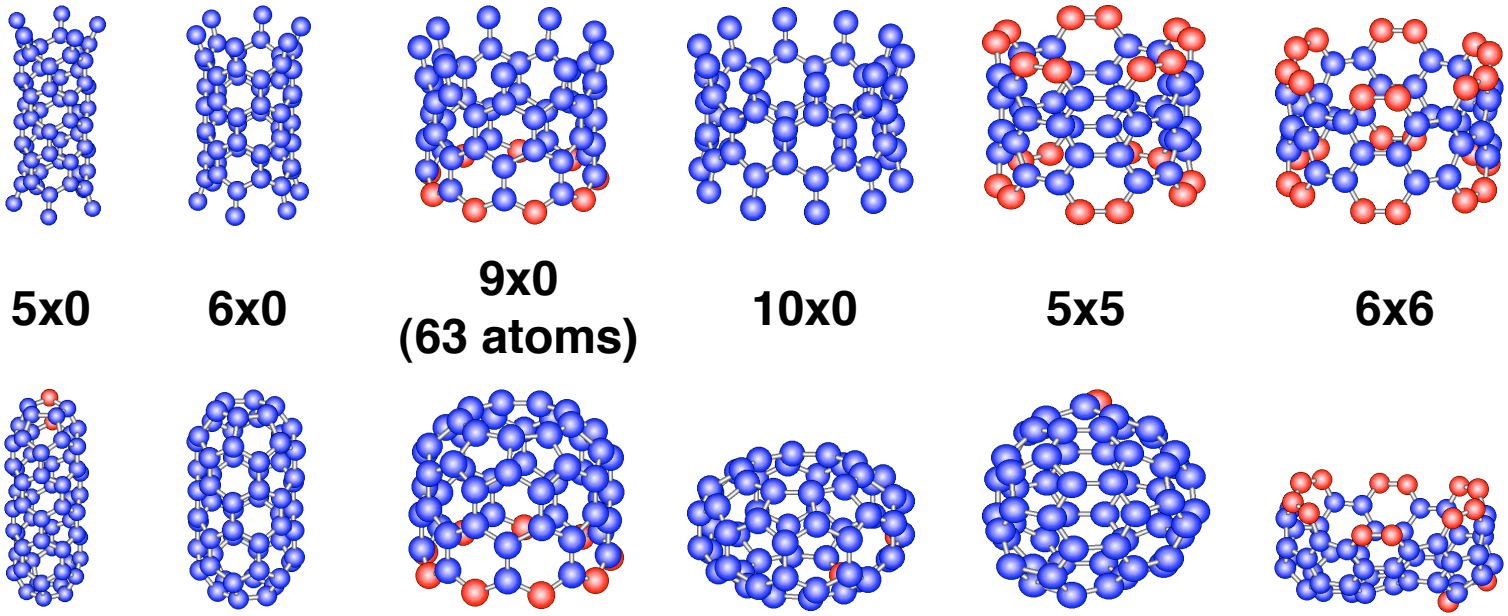
TAD: More 60-atom Nanotube Fragments

T=1500K (High T = 3000K), after first 1000 transitions

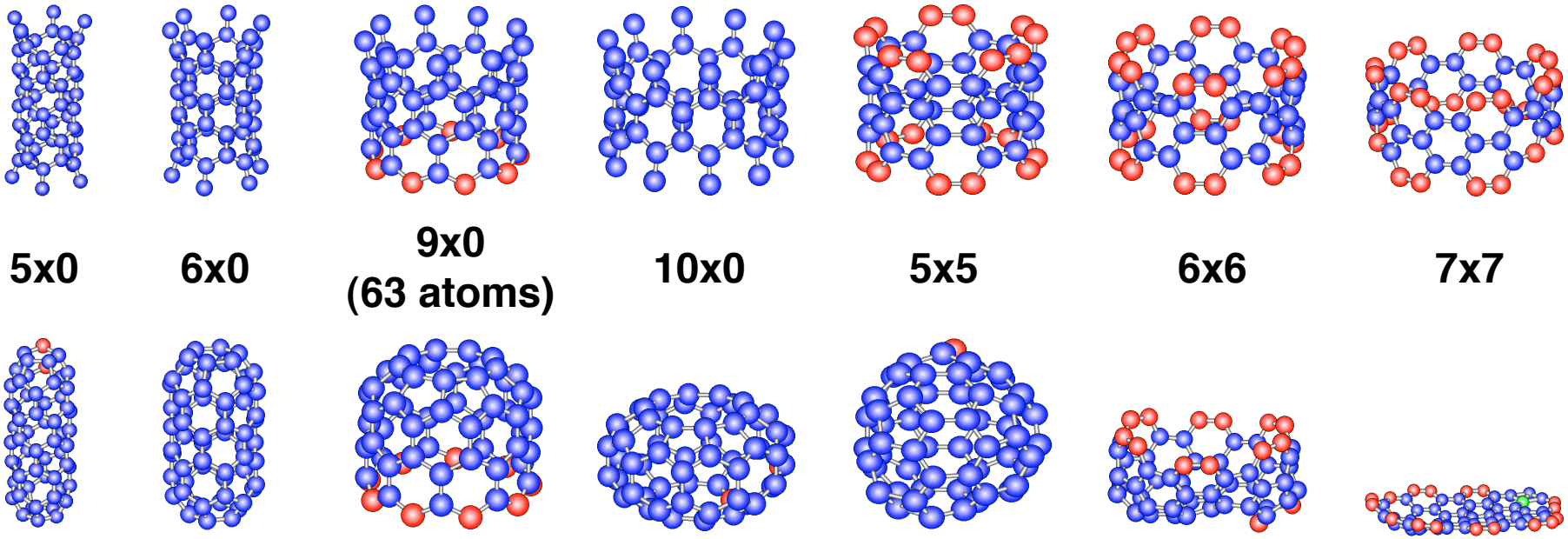


5x0	6x0	9x0 (63 atoms)	10x0	5x5	6x6
Total Simulation Time (fs)					
59	20	2.7	0.2 (133 states)	4	3
Boost					
1445	796	80	7	108	100

Uberuaga et al, to be published.

TAD: More 60-atom Nanotube Fragments

T=1500K (High T = 3000K), after first 1000 transitions

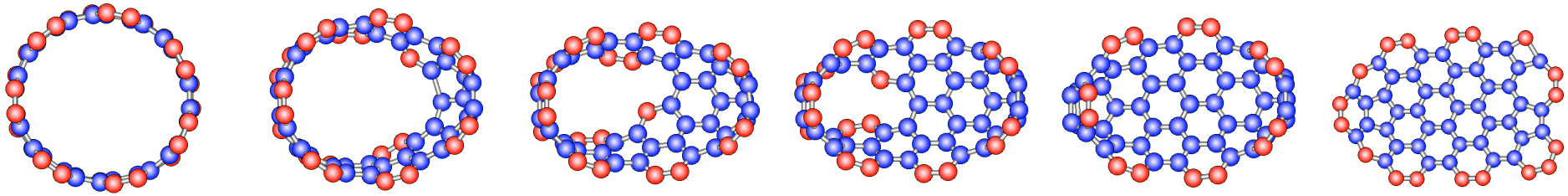


5x0	6x0	9x0 (63 atoms)	10x0	5x5	6x6	7x7
Total Simulation Time (□s)						
59	20	2.7	0.2 (133 states)	4	3	1
Boost						
1445	796	80	7	108	100	29

Uberuaga et al, to be published.

Slice of a 7x7 nanotube evolved with TAD

High Temperature: 3000K
Low Temperature: 1500K



t=0 time -----> 8.5 □s

Metastable flat structure is ~25 eV above energy of buckyball.
Kinetics is not the same as thermodynamics.

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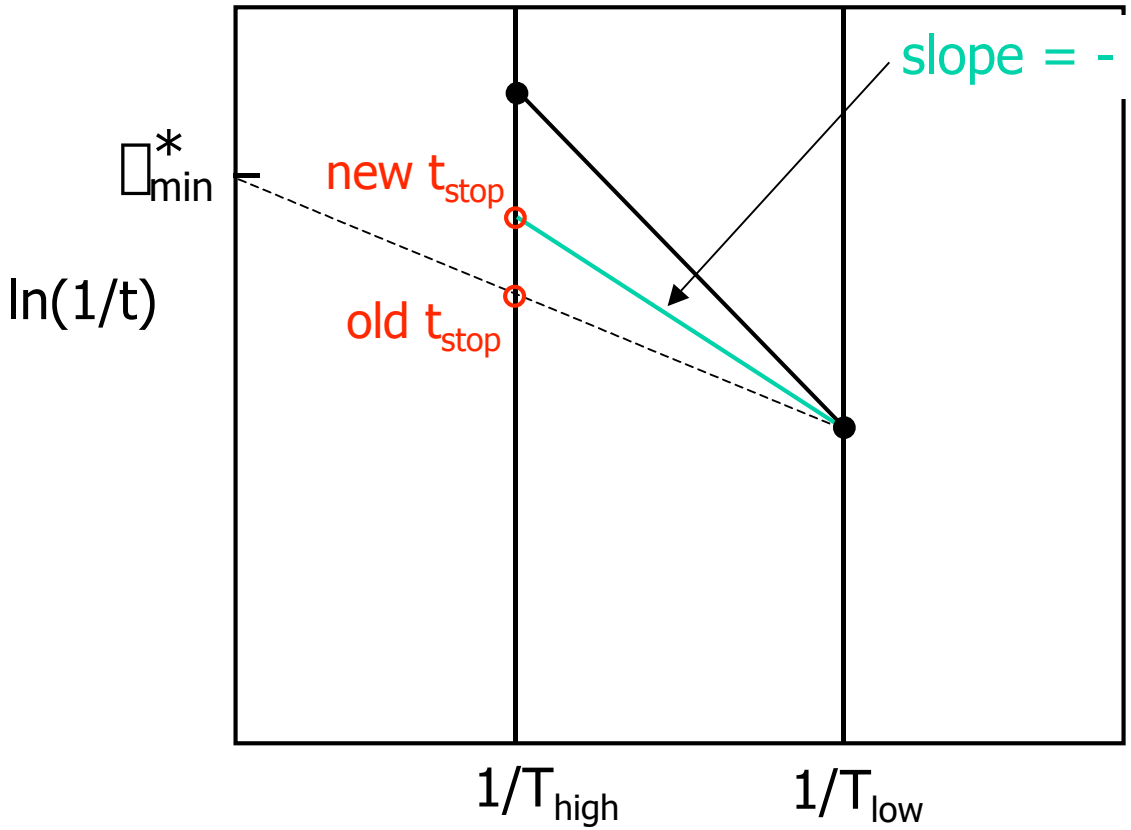
Using minimum barrier to stop TAD sooner

Assume we know the minimum barrier (ΔE_{min}) for escape from this state



"ETAD"

F. Montalenti and AFV, J. Chem. Phys. 116, 4819 (2002).

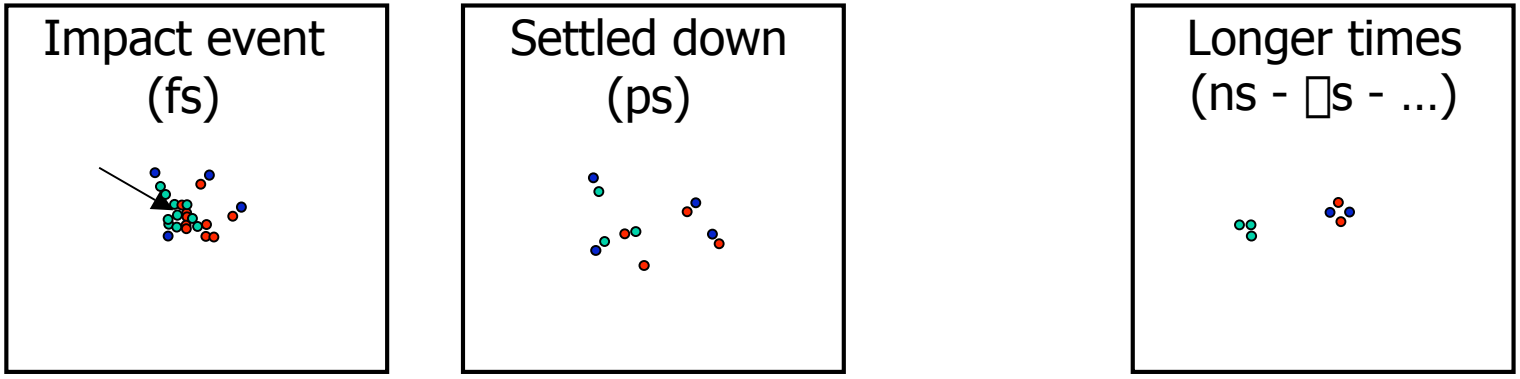
Combining dimer method with TAD

Dimer-TAD

- Use dimer method (Henkelman and Jonsson, 1999) to find a number of saddles and assume the lowest barrier (ΔE_{min}) is among them
- Supply this ΔE_{min} to ETAD for this state

----> accuracy of TAD (unless lowest barrier missed), with roughly the speed of the dimer method

MgO Radiation Damage Annealing



Buckingham coulombic pair potential

Molecular dynamics (MD) to simulate knock-on event and cascade. System settles down (becomes thermal) in a few ps.

Dimer-TAD to follow diffusive events from then on: ns, □s, ms, s, …

- diffusion of interstitials
- formation of interstitial dimers (e.g., Mg-O)
- diffusion of dimers to form larger clusters, etc.

Uberuaga, Smith, Cleave, Montalenti, Henkelman, Grimes, Voter, and Sickafus, Phys. Rev. Lett., in press (2004).

MgO - behavior of simple defects

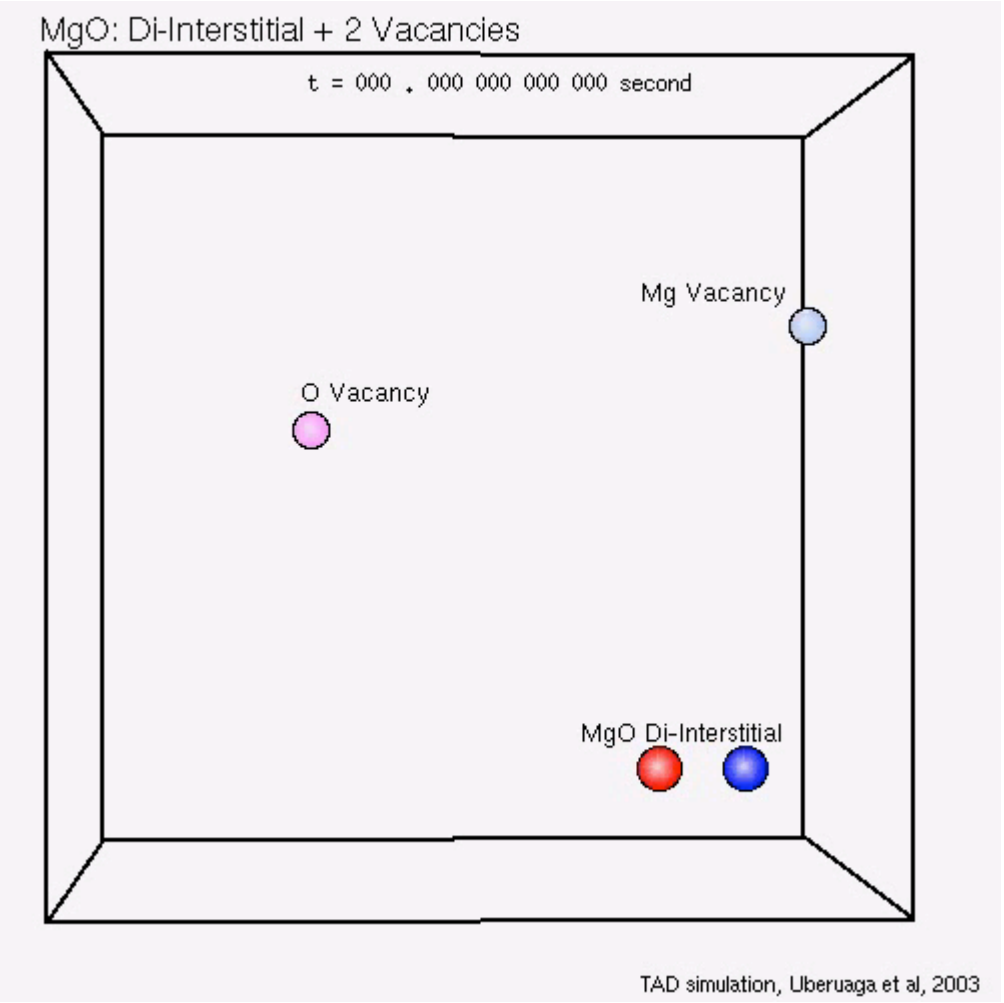
Vacancies are immobile (barrier > 2 eV)

Interstitials diffuse on ns-□s time scale

Interstitials are charged; attracted to either
oppositely charged vacancy (causing annihilation)
or oppositely charged interstitial (forming dimer)

TAD Simulation: Di-interstitial-vacancy annihiliation

- Begin with interstitial dimer (I_2) and two vacancies
- Each vacancy picks off one interstitial
- Long range, concerted events



Uberuaga, Smith, Cleave, Montalenti, Henkelman, Grimes, Voter, and Sickafus, Phys. Rev. Lett., in press (2004).

Growth of interstitial clusters

Interstitials diffuse on ns-□s time scale

Oppositely charged interstitials (O^{2-} + Mg^{2+}) join to form dimer

Dimers diffuse on s time scale

Dimers can encounter other interstitials and dimers to form larger clusters

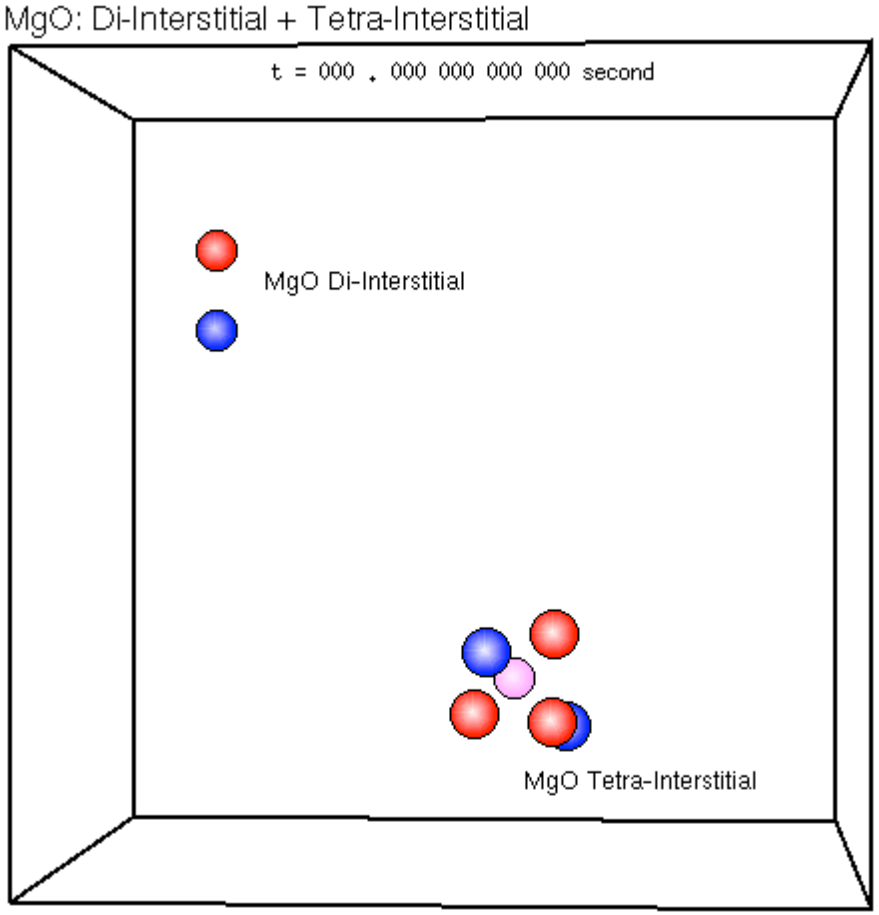
Two dimers form tetramer, which is immobile and stable to dissociation.

However, dimer plus tetramer can form a mobile hexamer species…

Uberuaga, Smith, Cleave, Montalenti, Henkelman, Grimes, Voter, and Sickafus, Phys. Rev. Lett., in press (2004).

TAD Simulation: dimer + tetramer interstitials

- In this case, dimer + tetramer forms hexamer in metastable state
- Metastable hexamer exhibits fast one-dimensional diffusion!
  - ns timescale
  - diffusion is 1D along <110>
  - decay to ground state takes years



TAD simulation, Uberuaga et al, 2003

Uberuaga, Smith, Cleave, Montalenti, Henkelman, Grimes, Voter, and Sickafus, Phys. Rev. Lett., in press (2004).

Summary

- Accelerated dynamics concept:
  - Let the trajectory find an appropriate way out of the state, but coax it into doing so more quickly
- Parallel Replica Dynamics
  - Exact dynamcs for infrequent-event systems
  - Very general
- Temperature accelerated dynamics
  - Controlled, testable approximations (harmonic TST, minimum prefactor)
  - large boost factor when barriers much higher than T

Review: Voter, Montalenti, and Germann, Ann. Rev. Mater. Res. 32, 321 (2002)

Web site: http://www.t12.lanl.gov/home/afv/